Methane Hydrate:
A Surprising Compound

WHAT do you get when you combine water and swamp gas under low temperatures and high pressures? You get a frozen latticelike substance called methane hydrate, huge amounts of which underlie our oceans and polar permafrost. This crystalline combination of a natural gas and water (known technically as a clathrate) looks remarkably like ice but burns if it meets a lit match.

Methane hydrate was discovered only a few decades ago, and little research has been done on it until recently. By some estimates, the energy locked up in methane hydrate deposits is more than twice the global reserves of all conventional gas, oil, and coal deposits combined. But no one has yet figured out how to pull out the gas inexpensively, and no one knows how much is actually recoverable. Because methane is also a greenhouse gas, release of even a small percentage of total deposits could have a serious effect on Earth's atmosphere.

Research on methane hydrate has increased in the last few years, particularly in countries such as Japan that have few native energy resources. As scientists around the world learn more about this material, new concerns surface. For example, ocean-based oil-drilling operations sometimes encounter methane hydrate deposits. As a drill spins through the hydrate, the process can cause it to dissociate. The freed gas may explode, causing the drilling crew to lose control of the well. Another concern is that unstable hydrate layers could give way beneath oil platforms or, on a larger scale, even cause tsunamis.

Lawrence Livermore's William Durham, a geophysicist, began studying methane hydrate several years ago with Laura Stern and Stephen Kirby of the U.S. Geological Survey in Menlo Park, California. With initial funding from NASA, they looked at the ices on the frigid moons of Saturn and other planets in the outer reaches of our solar system. One of these ices is methane hydrate.

Their work on the physical properties of this plentiful but poorly understood material has put the team in the forefront of methane hydrate research in the U.S. While they continue to study icy moons, Laboratory Directed Research and Development funding allows them to focus on applications that their research might have closer to home. In the process, they have run across a few surprises.

(a) Pressure = 27.6 MPa; temperature = 275 K.

(b) Pressure = 4 MPa; temperature = 275 K.

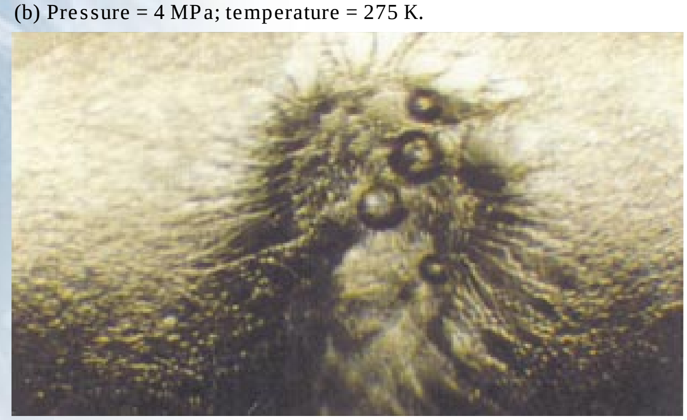

Figure 1. Partially reacted grains of methane hydrate that still contain cores of solid water ice and the same grains after the ice has begun to melt. In (a), the reaction proceeds rapidly as the hydrate mantle thickens and consumes the ice core. In (b), the rate of hydrate formation slows to almost zero. Melting of the superheated ice cores, apparently suppressed in (a) by rapid hydrate formation, is allowed to proceed. The grains become misshapen as liquid pools inside, causing distortion and partial collapse of the outer hydrate mantle within 10 minutes. Liquid water is radially expelled along fissures and crystallized as fine crystalline hydrate to surround the original grains.

Ice That Doesn't Melt

For their research, Durham, Stern, and Kirby needed good-quality samples of methane hydrate. But samples of the real thing are tough to acquire, requiring expensive drilling and elaborate schemes for core recovery and preservation. Previously developed methods for synthesizing the stuff in the laboratory generally resulted in an impure material still containing some water that had not reacted with the methane.

The Livermore–USGS team attempted an entirely new procedure. They mixed sieved granular water ice and cold, pressurized methane gas in a constant-volume reaction vessel and slowly heated it. Warming started at a temperature of 250 kelvin (K) (–10°F) with a pressure of about 25 megapascals (MPa).* The reaction between methane and ice started near the normal melting point of ice at this pressure (271 K, or 29°F) and continued until virtually all of the water ice had reacted with methane, forming methane hydrate.

The team studied the resulting material by x-ray diffraction and found pure methane hydrate with no more than trace amounts of water. This simple method produced precisely what they needed: low-porosity, cohesive samples with a uniformly fine grain size and random crystallographic grain orientation.

Says Durham, "In a way, we got lucky. We used the same technique we use for producing uniform water ice samples from 'seed' ice. We tried adding pressurized methane gas and heating it. And it worked."

It worked, but some unexpected things happened along the way. The ice did not liquefy as it should have when its melting temperature was reached and surpassed. In fact, methane hydrate was formed over a period of 7 or 8 hours, with the temperatures inside the reaction vessel reaching 290 K (50°F) before the last of the ice was consumed. Repeated experiments produced the same result: ice that did not melt (Figure 1).

A control experiment replaced the methane with neon, which does not form the cagelike latticework of gas and water molecules that is a gas hydrate. Under otherwise identical experimental conditions, the ice melted as it should. Other experiments replaced the methane with both gaseous and liquid carbon dioxide, which does form a hydrate. Here the superheating phenomenon reappeared, indicating that it is not unique to methane hydrate.

Durham and his team believe the superheating phenomenon is related to active hydrate formation. The reaction at the free ice surface somehow suppresses the formation of a runaway melt. Figure 1 shows that when the reaction ceases, melting happens immediately. The American Chemical Society was impressed enough with these rather bizarre results to give the team a cash prize and award in late 1997.

Another Surprise

Once the team had large, pure samples they could work with, they began studying the material's physical properties and the way it forms and dissociates. This is research at its most basic. But its applications are clear when one considers that dissociation of seabed methane hydrate deposits could cost the lives of workers on an oil drilling platform.

Methane hydrate's stability curve (Figure 2) has been established for some time. If conditions fall outside that curve, the material will dissociate into its components, methane and water. Durham, Stern, and Kirby looked at how the dissociation occurs under a variety of temperature and pressure conditions outside the curve.

After the samples were created, the pressure was reduced to 0.1 MPa, the pressure at sea level. They did this in two ways: by slow cooling and depressurization and by rapid depressurization at a range of temperatures.

The compound decomposed to ice and gas as expected in all experiments except those that involved rapid depressurization at temperatures from 240 to 270 K (Figure 3). In these experiments, the team found yet another surprise. Even after the pressure drop, the methane hydrate was "preserved" as a compound for as long as 25 hours before it decomposed.

This behavior may have implications for future exploitation of the material. Preserving the mixed hydrates may be possible at an easily accessible temperature, just a few degrees below ice's melting temperature.

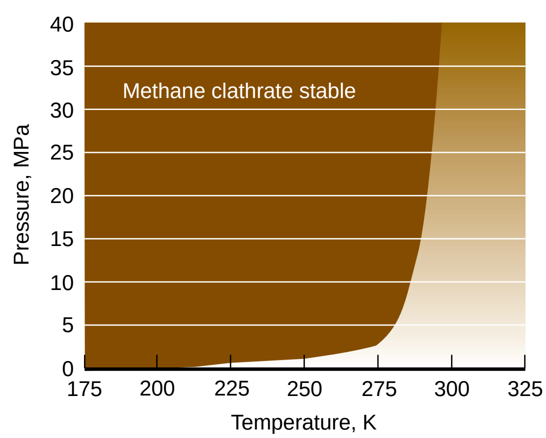

Figure 2. The stability curve shows that methane hydrate is stable at 0.1 MPa if temperatures are low enough and that it is stable far above the melting point of water ice if pressures are high enough.

* 0 K is absolute zero. At 0.1 MPa (1 atmosphere), water freezes at 273 K and boils at 373 K.

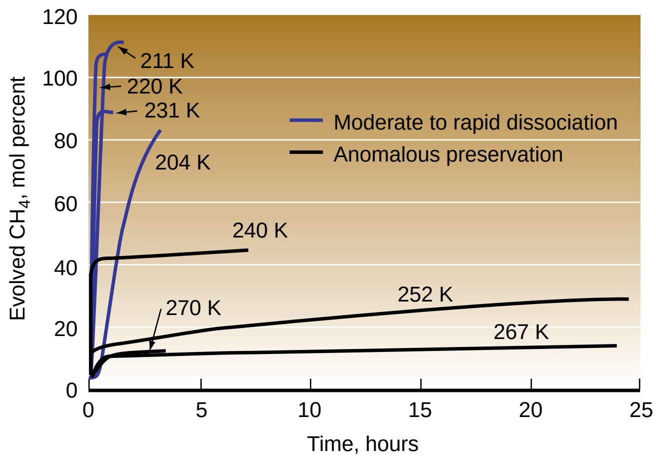

Figure 3. At lower temperatures (the blue lines), methane hydrate dissociates rapidly after rapid depressurization. At warmer temperatures (the red lines), dissociation is complete only after periods as long as 25 hours.

Figure 4. Used to compare the strengths of water ice and methane hydrate, a sample containing both was subjected to axial stress from a piston inside a cryogenic container about 25 millimeters in diameter. Inside this vessel, the weaker water ice (toward left of photo) deforms, causing a bulge, while the stronger methane hydrate under the same stress does not bulge.

In another series of experiments, the team is looking at the strength of gas hydrate samples in various temperature and pressure scenarios. Results of these experiments may indicate the possible effects that stresses from gravity, tectonic activity, or human disturbance might have on gas hydrate deposits.

Thus far, the team has found that water ice and methane hydrate have about the same strength at very low temperatures of 180 K and below. But the hydrate is much stronger than ice at temperatures of 240 K and above. The most recent data indicate that methane hydrate is several times stronger than ice (Figure 4). Although methane hydrate is not as strong as rock, the data may be good news for the stability of the deposits.

More Work Ahead

Plenty of work remains to be done. The team plans to measure the molecular diffusion of gases through methane hydrate and to study special compounds that might suppress the formation of hydrates in cold pipelines. They also will do experiments to measure methane hydrate's thermal properties. Says Durham, "We already know that it is a very poor conductor of heat. If you hold a piece of it in your hand, it doesn't feel like ice at all. It almost feels like styrofoam."

A new heat exchanger installed in December at Livermore's ice physics laboratory allows Durham to heat samples from 180 to 260 K in about an hour, a process that used to take 24 hours. Durham notes, "Now we can do experiments much more quickly and thus can run a lot more experiments. Methane hydrate is a material with plenty of surprises, so there is no telling what we might discover next."

—Katie Walter

Key Words: clathrate, energy sources, gas hydrates, methane hydrate, global climate, superheating.

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LATIS Modeling Laser Effects on Tissue

LASER beams—used for swashbuckling effect in the movie *Star Wars* nearly a quarter century ago—are now proving an effective weapon in the war against medical conditions such as stroke and arthritis, as well as in surgical procedures. A critical ally in this battle is LATIS (an acronym for LAser-TISsue), a computer code developed at Lawrence Livermore. It is a two-dimensional, time-dependent code that simulates the interaction of laser light with living tissue. LATIS is based on experience gained during 25 years of modeling high-intensity laser–matter interactions for inertial confinement fusion.

Medical researchers from the Department of Energy's national laboratories, as well as from universities and industry, have been turning to LATIS and its new, three-dimensional counterpart, LATIS3D, for help in the design and use of new laser medical tools. LATIS was originally developed by Livermore physicists Richard London, George Zimmerman, David Bailey, and Mike Glinsky (now at Shell Co.). The codes are particularly useful in analyzing novel laser systems used for photothermal, photochemical, and photomechanical applications.

For these medical applications, LATIS explores laser-light propagation, thermal heat transport, material changes such as thermal coagulation and photochemistry, and hydrodynamic motion. "LATIS was originally funded as part of a Laboratory Directed Research and Development project looking at ways to diagnose and treat stroke," London explains. "In developing the code, we leveraged experience, expertise, and technologies already available at the Laboratory in areas such as computational modeling, laser technologies, and precision engineering of laser–matter interaction and radiation hydrodynamics. The results are having an effect on healthcare technologies and economics by making it easier—and less expensive—to develop some of these laser tools."

In the past three years, LATIS codes have simulated a laser system that will break up blood clots in stroke patients and experiments using a tissue "welding" system based on laser light. Current work includes a new technique for easing arthritis.

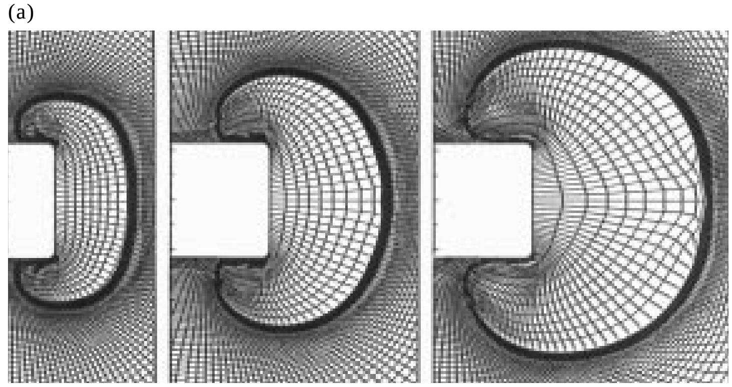
Attacking Strokes at the Source

Strokes, like heart attacks, usually result from decreased blood flow interrupting the supply of oxygen and nutrients to tissue. Most frequently, the flow is decreased because of a blockage in blood vessels.

In 1995, Livermore's stroke-initiative team began developing optical therapies for breaking up clots in the blood vessels of the brain as well as the laser–tissue interaction modeling that was the beginning of LATIS (for more information see *S&TR*, June 1997, pp. 14–21). The clot-busting system delivers low-energy laser pulses through a fiber-optic microcatheter positioned close to the cerebral clot. The optical light is converted to acoustic stress waves that break up the clot and restore blood flow in the cerebral arteries.

"With LATIS, we simulated the interaction of the laser beam with fluids (blood, saline solution), the blood clot, and tissue near the end of the fiber. We then compared the results with experiments," London said (Figure 1). "We modeled the generation of acoustic waves near the interaction and the

(a)



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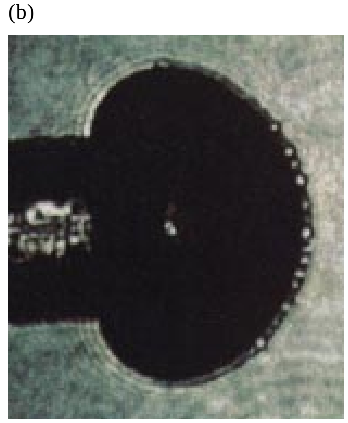

Figure 1. Sophisticated two-dimensional computer simulations made with LATIS by Peter Amendt predicted experimental behavior for a device that breaks up stroke-inducing blood clots using laser energy converted into acoustic energy. (a) Two-dimensional simulation of bubble dynamics, showing a "special zoning scheme" that is also potentially useful for laser fusion modeling. (b) Close-up of a bubble generated in experiments.

acoustic energy on the blood clot. The results provided direction to researchers on the optimal parameters for laser wavelength, pulse length, and optical fiber diameter. The modeling also helped reduce the number of experiments needed."

LATIS incorporated a number of variables—the size and composition of the clot, strength of the blood-vessel tissue, and buildup and transport of heat during laser clot-busting. The code then numerically simulated the hydrodynamics of the laser-created energy and predicted the energy needed to break up the clots without damaging other tissue.

This clot-busting instrument, now being advanced by Endovasix Inc., is entering clinical tests and should be commercially available within a couple of years.

Modeling Temperatures for Tissue Welding

In another effort spearheaded by Livermore's Medical Photonics Laboratory, researchers, led by Duncan Maitland, designed a system that uses laser light to join tissue, much like sutures. The laser energy activates tissue bonds between surgical surfaces, fusing them together. If there's too much heat, however, the tissue is damaged, and poor healing results. If there's not enough heat, the bonds don't form.

In this case, LATIS helped researchers analyze data from tissue experiments and then design the system. LATIS modeled the heating effects and the heat transport of the laser energy absorbed by the tissue. The researchers made interesting discoveries in this modeling effort. For instance, for a pulse of many seconds to a few minutes, they found that the evaporation of water from the surface of the tissue cools the tissues, much like sweating. Before this, no one had determined quantitatively how important cooling was to the process. They also simulated the temperature profile of the underlying tissue, something that wasn't possible to measure experimentally. The findings had a significant impact on the system's design.

LATIS modeled the in-depth temperature profile for two temperature-control techniques: one, by dripping water on the tissue surface, the other by using a feedback system incorporating an infrared thermometer, developed at the Laboratory, that

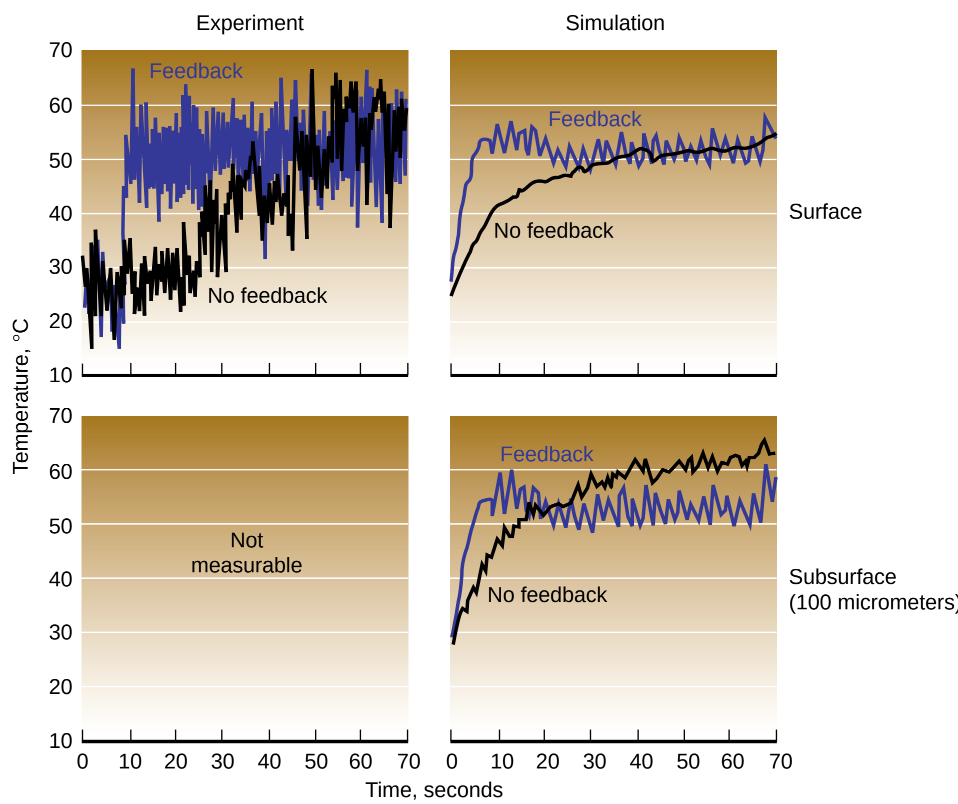

Figure 2. Numerical simulations performed with LATIS by David Eder suggested that the improved results of the tissue-welding technique are related to better control of the temperatures below the surface of the tissue. Such control was provided by a temperature sensor/feedback system developed at Lawrence Livermore's Medical Photonics Laboratory.

controls the amount of laser energy delivered to the tissue surface (see *S&TR*, October 1998, pp. 14–15). Both methods cool the surface of the tissue, but the question was which method better controls the temperature below the surface.

"The modeling predicted that temperatures below the surface would stay more uniform with the feedback system," said London (Figure 2). "The experimental results showed that the welds using the feedback technique were superior in several ways. The only way the techniques differed was in their in-depth temperature profiles."

The resulting tissue-welding system is showing particular promise in heart surgery on newborns, and the Laboratory is collaborating with the University of California's San Francisco Medical Center and Conversion Energy Enterprises on experiments to eventually bring this system to market.

Easing Arthritis

Another medical application for advances of the LATIS code is photodynamic therapy, using light-activated drugs to treat medical conditions including cancer and arthritis.

As part of the Center for Excellence for Laser Applications in Medicine, formed in 1998 by the Laboratory and the University of California at Davis's Medical Center, researchers are developing a treatment for arthritis based on photodynamic techniques. This project correlates with a Laboratory Directed Research and Development project to develop a successor to LATIS—a three-dimensional interactive code called LATIS3D. It is being used to make an accurate calculation of the distribution of laser light in a joint.

"We set up a model of the geometry of a knee joint, which is a very complicated three-dimensional (3D) structure," said London. "Developing a numerical description of the joint required making a three-dimensional numerical mesh, or grid. We are using magnetic-resonance images—MRIs—of knee joints as a basis for our 3D model. We will then define the properties of each tissue in each mesh."

With the model in place, the team uses Monte Carlo probability methods to determine light distribution in the various tissues. "We calculate where the light goes. Combining that with estimates from our collaborators of where the drug is concentrated, we can then calculate how the tissue is affected," said London.

These modeling efforts will help in designing the photodynamic therapy instrument, determining the laser energies needed, and positioning the light source.

For this application, LATIS3D could also be used to develop physician treatment plans. A physician can transfer a patient's MRI data into the model and come up with a plan that includes where to place the fiber, how long to make the exposures, how much energy is needed, and so on.

Powerful Modeling Tool Meets the Medical Future

Developing new instruments and procedures for use in laser medicine typically involves extensive experimental and clinical studies. As London noted, computational modeling codes such as LATIS and LATIS3D can help medical researchers define experimental parameters more narrowly and gain deeper understanding of specific laser medical processes. LATIS will also have a future role in designing patient-specific treatment plans and in training physicians.

"In these ways," said London, "modeling can lead to more rapid development of new medical systems, to the genesis of new ideas, and to more individually tailored treatment plans. All, of course, to the ultimate benefit of patients."

—Ann Parker

Key Words: arthritis, laser surgery, laser–tissue interaction modeling, LATIS code, LATIS3D code, stroke, tissue welding.

For further information contact Rich London (925) 423-2021 (london2@llnl.gov), or see the Livermore Medical Technology Program's Web site at http://lasers.llnl.gov/lasers/mtp/modeling.html.